The potential value of biochar in the mitigation of gaseous emission of nitrogen

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HIGHLIGHTS

- Biochar and dicyandiamide (DCD) effects on N transformation and losses were studied.
- DCD decreased N_2O emission from N sources applied soil but increased NH_3 emission.
- Although DCD significantly reduced N_2O emission, biochar decreased total N loss by 25%.
- Biochar can replace chemical nitrification inhibitors thereby mitigating gaseous N loss.

GRAPHICAL ABSTRACT
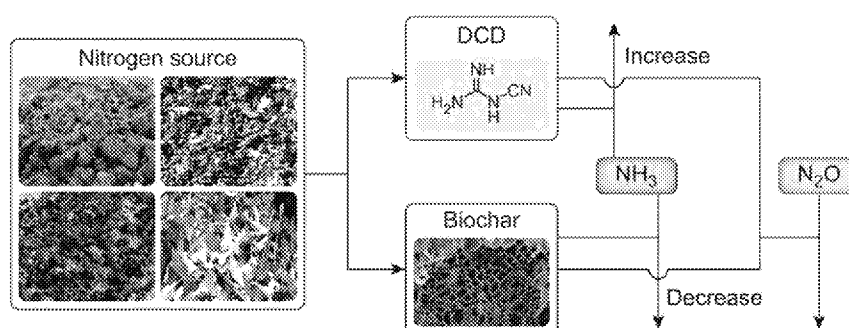
ARTICLE INFO

ABSTRACT

Nitrogen (N) losses through gaseous emission of ammonia (NH_3) and nitrous oxide (N_2O) can contribute to both economic loss and environmental degradation. This study examined the effect of biochar and a chemical nitrification inhibitor, dicyandiamide (DCD), on N transformation and N losses via gaseous emission of NH_3 and N_2O from agricultural soils treated with a range of organic and inorganic N sources. The addition of DCD reduced N_2O emission from both organic and inorganic N sources treated soils by 75%, but increased ammonium (NH_4^+) concentration and subsequently induced high NH_3 emission from the soils. In contrast, the addition of biochar reduced both N_2O and NH_3 emissions from organic and inorganic N sources treated soils by 23% and 43%, respectively. The effectiveness of biochar and DCD in reducing NH_3 volatilization and N_2O emission depends on the nature of the N sources and their initial mineral N concentration. The study demonstrated that biochar can be used to mitigate N losses resulting from NH_3 volatilization and N_2O emission.

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1. Introduction

An upsurge of interest in gaseous losses of nitrogen (N) as ammonia (NH_3) and nitrous oxide (N_2O) from soil has occurred during recent decades because of the environmental impacts of these losses. Strategies of regulating the fate and behavior of N in agricultural systems focus mainly on improving the nutrient use efficiency of fertilizer N and reducing environmental N pollution. In addition, farmers are facing significant economic loss due to poor growth yield caused by N loss as NH_3 and N_2O emissions. Increasingly, the use of inhibitors with N fertilizers is becoming an important strategy for the sustainable management of nutrients in agricultural production. Nitrification inhibitors (NIs) reduce N_2O flux from N fertilizers (Di and Cameron, 2008), urine deposits in pasture systems (De Klein et al., 2011; Luo et al., 2013), and organic manures (Asing et al., 2008; Li et al., 2014), but they are reported to increase NH_3 volatilization losses (Zaman et al., 2008). This increase in NH_3 volatilization may negate the beneficial effects of NIs on the reduction in N_2O emission (Singh et al., 2010). Dicyandiamide (DCD) is the most extensively studied and used NI because it is highly effective in inhibiting nitrification and reducing N_2O emissions. Most studies involving DCD in reducing N losses as N_2O have focused on its value in enhancing fertilizers in pasture systems, but little research has investigated its effect on N gaseous losses (NH_3 and N_2O) from various N sources in agricultural soil. It is essential to understand the influence of DCD on both NH_3 and N_2O emissions in relation to the quantity of added N in order to retain more N in the soil-plant system.

In recent years, biochar has received increasing attention because of its agronomic benefits (Sohi et al., 2010) and influence on carbon (C) and N transformations in soils (Clough and Condron, 2010; Spokas et al., 2012). For example, biochar addition has been shown to impact NH_3 volatilization (Steiner et al., 2010), N-leaching (Singh et al., 2010), and N_2O emissions (Spokas et al., 2009; Van Zwieten et al., 2010). The ability of biochar in reducing NH_3 volatilization due to its sorption capacity has been known for some time (Holmes and Beebe, 1957). Seredych and Bandosz (2007) have recorded a range of NH_3 sorption capacities (<1 mg NH_3/g for non-oxidized biochars to >60 mg NH_3/g for oxidized biochars). Several laboratory and field studies have documented the suppression of N_2O emissions by biochar addition to soils (Clough and Condron, 2010; Singh et al., 2010). For example, Rondon et al. (2005) noticed 80% and 50% reduction in N_2O emissions when biochar was added to grass and soybean systems, respectively. Most studies investigated the effect of biochar in reducing NH_3 and N_2O emissions separately. However, the influence of biochar on both NH_3 and N_2O emissions should be simultaneously evaluated to properly assess N retention in the soil-plant system.

The objective of this study was to compare the effects of biochar and DCD on the fate and behavior of various N sources (organic and inorganic) in an agricultural soil. The specific objectives were to: (i) examine the effect of biochar and DCD application on mineral N transformations in soil amended with various organic amendments (OAs) and urea, (ii) study the influence of biochar and DCD on N gaseous losses (NH_3 and N_2O) from soil receiving urea and various OAs, and (iii) compare and assess the effectiveness of biochar and DCD in reducing total N loss from soil receiving various N sources.

2. Materials and methods

2.1. Soil, nitrogen sources, DCD, and biochar

Fresh soil used in this study was collected from an agricultural field in Port Wakefield, South Australia (34.157751°S; 137.787201°E). Soil was identified as Andisol in Australia soil classification. The N sources include horse manure (HM), sheep manure (SM), blood and bone mix (BB), cow manure (CoM), green waste compost (GWC), biosolids (BS), chicken manure (CM), and urea. Commercially available DCD (99%) obtained from Alfa Aesar (Massachusetts, USA) was used in this study.

Biochar produced from macadamia (*Macadamia tetraphylla*) nut shell at pyrolytic temperature of 465 °C was used in this study. Physicochemical properties of the biochar are detailed in Table 2. Biochar-Milli-Q (MQ) water mixture (1:10 ratio- dw/v) was shaken in an end-over-end shaker for 1 h, and analyzed for pH and EC using smartCHEM-LAB Laboratory Analyser. To quantify dissolved organic carbon (DOC), biochar was shaken with MQ water (1:10 ratio- dw/v) for 3 h in a horizontal shaker, centrifuged at 3000g for 20 min, and filtered using 0.45 μm syringe filter. The filtrate was analyzed for total dissolved inorganic carbon (TIC) in an automated TOC analyzer (Shimadzu TOC-LCSH, Kyoto, Japan). Total C and N were determined by combustion of 0.25 g of oven dried and ground biochar sample at 1100 °C in a Leco C/N analyzer (Leco TruMac® CNS/NS, USA).

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to measure total elemental composition of biochar (P, K, and S) after microwave digestion of 0.1 g of oven dried biochar with 4 ml 69% HNO_3 and 1 ml 33% H_2O_2 (Sparks et al., 1996). Specific surface area (Brunauer–Emmett–Teller, BET) and pore volume (Barrett–Joyner–Halenda, BJH) of biochar were determined using a Quantachrome NOVA (Quantachrome Instruments, USA) 1000e Analyzer by adsorbing/desorbing N_2 at 77 K on/from the samples previously dried and out-gassed at 160 °C for 16 h.

Soil and amendment characteristics are presented in Table 1. The pH values of the OAs ranged from 6.84 to 9.09, C:N ratios ranged from 5 to 14, and mineral N concentrations varied widely from 23 mg N/kg to 33,379 mg N/kg. The blood and bone mix had the lowest pH value, and CM had the highest pH value. The soil had a pH of 7.99, C:N ratio of 24, and mineral N concentration of 99 mg N/kg soil. The biochar had a pH of 10.08, C:N ratio of 113, and mineral N concentration of 28.93 mg N/kg soil. The NH_4^+-N concentration was below the detectable limit. Biochar showed a specific surface area of 104.68 m^2/g with a low pore volume of 0.085 cm^3/g (Table 2).

2.2. Experiments

Two sets of experiments were conducted to separately examine the effect of biochar and DCD on N transformation (Experiment 1) and N gaseous losses (Experiment 2) in soils treated with a range of OAs and urea. The treated soils were incubated in dark at field capacity at a room temperature ranging from 18 to 21 °C for 51 days.

In both experiments, 18 treatments with three replicates as described below were studied. Nine treatments with N sources at 300 mg N/kg soil and biochar at 7.18 mg C/kg soil (Singh et al., 2010) included the following: Soil with biochar; Soil with HM and biochar; Soil with SM and biochar; Soil with BB and biochar; Soil with CoM and biochar; Soil with GWC and biochar; Soil with BS and biochar; Soil with CM and biochar; Soil with urea and biochar. Similarly, nine treatments with N sources at 300 mg N/kg soil and DCD at 25 mg/kg soil (Singh et al., 2008) were prepared and studied. For each treatment, 250 g soil was mixed thoroughly with the respective N sources, biochar, and OAs, and placed in plastic zip lock bags.

2.2.1. N transformation and pH

A sub-sample (5 g oven dry equivalent) from each treatment bag was extracted with 2 M KCl solution by shaking in an end-over-end shaker for 1 h (1:10 soil: extractant ratio). The extracts were analyzed for ammonium (NH_4^+) colorimetrically by the salicylate-nitroprusside method of Mulvaney (1996) on a Skalar autoanalyzer (Skalar UK Ltd., York, UK). Nitrate in the KCl extract was also determined colorimetrically using the same Skalar autoanalyzer in which a Cd–Cu column was used to reduce NO_3^- to NO_2^- (Jones et al., 2004). A sub-sample (1 g oven dry equivalent) from each bag was shaken with 10 ml of 0.01 M $CaCl_2$ in an end-over-end shaker for 1 h and measured for pH using a pH/conductivity meter (smartCHEM-LAB Laboratory Analyzer, VWR International Pty Ltd., Australia).

Table 1
Physiochemical properties of soil and amendments used in this study (mean ± standard deviation).

Sample	pH	Total C (%)	Total N (%)	C:N ratio	NH_4^+-N (mg/kg)	NO_3^--N (mg/kg)
HM	8.32 ± 0.01	11.29 ± 1.10	0.79 ± 0.07	14.2	160.21 ± 1.2	1325 ± 10.2
SM	8.22 ± 0.03	13.74 ± 0.41	1.65 ± 0.00	8.33	6094.1 ± 19	2782 ± 13.4
BB	6.84 ± 0.01	30.16 ± 0.29	5.85 ± 0.06	5.16	11,924 ± 22	51.02 ± 5.66
CoM	7.82 ± 0.02	25.59 ± 0.11	2.32 ± 0.02	11.0	2955 ± 9.09	21.14 ± 3.17
GWC	8.87 ± 0.03	17.10 ± 0.42	1.43 ± 0.03	11.9	118.2 ± 1.61	113.3 ± 6.27
BS	7.76 ± 0.04	17.20 ± 1.60	3.11 ± 0.10	5.53	33,056 ± 26	323.0 ± 9.30
CM	9.09 ± 0.10	26.00 ± 0.19	4.17 ± 0.02	6.24	12,877 ± 16	10,218 ± 25.6
Urea	–	20.40 ± 0.04	46.5 ± 0.04	0.44	–	–
Soil	7.99 ± 0.06	0.921 ± 0.02	0.04 ± 0.00	23.0	87.12 ± 1.06	12.14 ± 0.86

2.2.2. Gaseous emission

Experiment 2 also comprised of 18 treatments with 3 replicates for each treatment set up in specially designed bottles for gaseous (NH_3 and N_2O) measurement. Schott bottles (250 mL) fitted with a 3 way stop cock on the lid were used in this experiment. The bottles were filled with 100 g soil amended with and without N sources (at 300 mg N/kg soil), with biochar (at 7.18 mg C/kg soil)/with DCD (at 25 mg/kg soil). A short scintillation bottle with 0.1 M H_2SO_4 to capture NH_3 was hung inside the bottle with the support of a thread.

Ammonia trapped in H_2SO_4 was analyzed for total NH_4^+ as detailed in Section 2.2.1. Ammonia measurements were taken daily for 2 weeks from the beginning, followed by every other day for 3 weeks, and then twice a week until the end of the incubation period. After NH_3 measurements, the lids were removed and the bottles were kept open for 1 h to achieve equilibrium with ambient conditions.

Nitrous oxide measurement was conducted by collecting gas samples using a 10 ml gas-tight syringe (SGE Analytical Science, Texas, USA) after closing the bottle for 1 h. The gas samples were collected daily for the first 2 weeks to capture the immediate changes in gas fluxes, followed by alternate days for 3 weeks, and then twice a week until the end of the incubation period (51 days). The emissions for the days when no measurement was recorded were estimated by taking the average of the emissions before and after that day (Pathak and Nedwell, 2001). The gas samples collected were transferred to pre-evacuated vials (Labco Exetainers®, UK), and then analyzed for N_2O gas (mg/h) using an Agilent 1960A gas chromatography with 63Ni-Electron capture detector. Three bottles with no soil were also set up to measure the background/atmospheric NH_3 and N_2O. The samples collected from these empty bottles were used as a reference for calculating atmospheric NH_3 and N_2O gas flux.

2.2.3. Estimation of nitrification inhibition index

A nitrification inhibition index (NII) was calculated to indicate the effectiveness of biochar and DCD in N retention in soil, using the following formula (McCarty and Bremner, 1989) (Eq. (1)):

$$NII = \frac{N_C - N_N}{N_C} \times 100 \tag{1}$$

where, N_N and N_C are the NO_3^--N concentrations in the N sources added soils in the presence and absence of biochar or DCD (mg/kg N source), respectively.

2.2.4. N recovery

The N recovery from various components (NH_3 emissions, N_2O emission, and mineral N contents in the soil) was calculated using the following equation (Eq. (2)):

$$N_{recovery} = \left[\frac{N_P - N_C}{N_T} \right] \times 100 \tag{2}$$

where, N_P refers to the various N components (NH_3 emissions, N_2O emissions, and mineral N present in the soil at the end of incubation period, mg/kg soil) in the soil treated with organic and inorganic N sources with biochar or DCD; N_C refers to the corresponding N components in the treatments without N sources (mg/kg soil) (i.e., soil + biochar treatment or soil + DCD treatment); N_T refers to total N added to the soil as N source (mg/kg soil).

2.3. Statistical analysis

The mean values of NH_4^+-N, NO_3^--N, soil pH, NH_3-N, and N_2O-N were calculated from three replicates of each treatment, and analysis of variance (ANOVA) using SPSS software was performed on these results for mean comparison using Fisher's Least Significant Difference (LSD) at 5% significance. Regression analyses between NH_3 emission and soil pH and NH_4^+-N concentration, and between N_2O emission and NH_4^+-N concentration was also conducted using SPSS software (SPSS Inc., Chicago, USA).

3. Results and discussion

3.1. N transformation study

3.1.1. Ammonium concentration

In general, NH_4^+-N concentration increased during the first week of incubation with the commencement of ammonification reaction in both biochar and DCD treated soils (Fig. 1a and b). Hydrolysis of urea N ($CO(NH_2)_2$) and organic N in the fertilizer and OAs in the presence of urease enzyme produces NH_4^+ ions. The accumulation of NH_4^+ ions occurred during the first week of incubation as triggered by water addition (Eq. (3)).

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2 \tag{3}$$
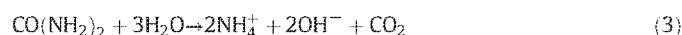
A small increase in soil NH_4^+-N concentration in the treatment with biochar or DCD only (no N source) was possibly due to mineralization of native soil organic matter (SOM) (Taghizadeh-Toosi et al., 2011) (Fig. 1a

Table 2
Physiochemical properties of biochar and DCD used in this study (mean ± standard deviation).

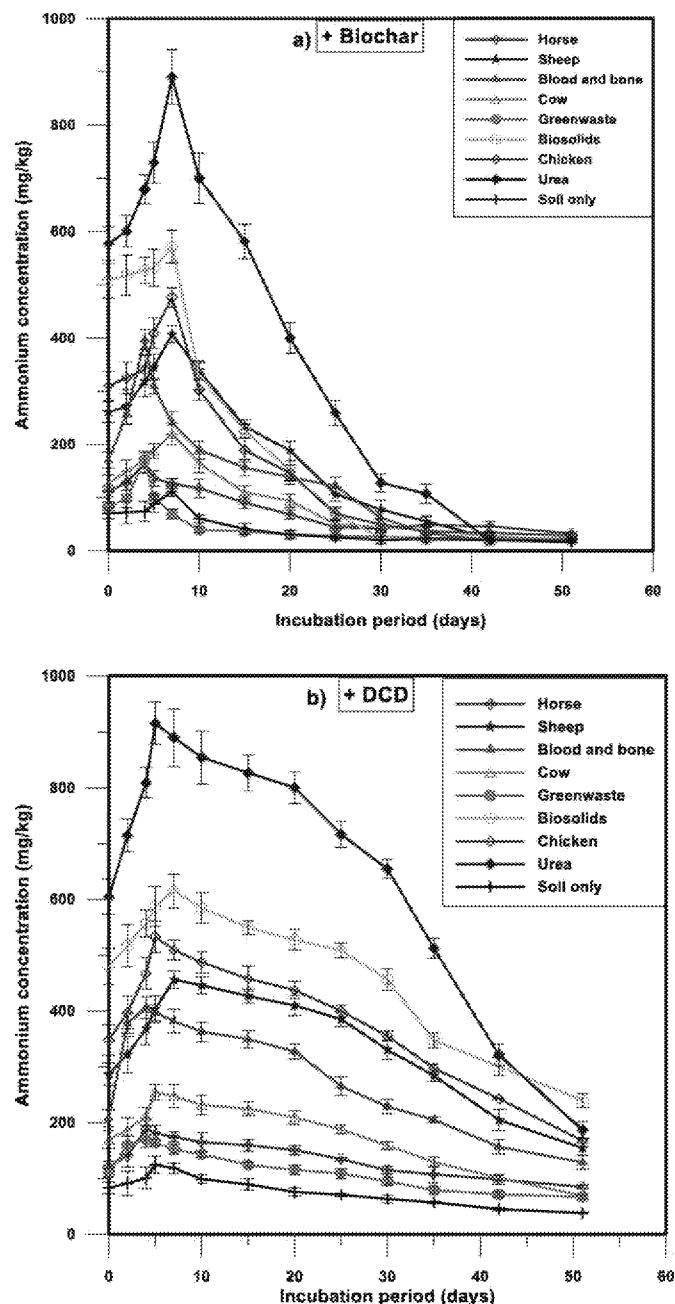|	pH	Total C (%)	Total N (%)	C:N ratio	NH_4-N (mg/kg)	NO_3^--N (mg/kg)	Specific surface area (m²/g)	Pore volume (cm³/g)	Pore size (nm)
Biochar	10.1	74.7	0.66	113	Nd	28.9	104	0.09	30.3
DCD	8.26	28.5	66.0	0.44	Nd	Nd	Nd	Nd	Nd

Nd – not detected.

Fig. 1. Ammonium-N concentrations in soils treated with organic and inorganic N sources in the presence of biochar (a) and DCD (b) over a period of 51 days. Each value represents a mean of three replicates with standard deviation shown by vertical bars.

and b). In the incubated soil samples, NH_4^+-N concentration followed in the order of Urea > BS > CM > SM > BB > CoM > HM > GWC, regardless of the addition of biochar or DCD. Ammonification was completed within 7 days of incubation as indicated by a decrease in NH_4^+-N concentrations after 7 days. This decline of NH_4^+-N concentration with time could be due to: 1) the commencement of nitrification (Fig. 2a and b), 2) NH_3 volatilization, and/or 3) microbial metabolization of NH_4^+ ions (Bhandral et al., 2007; Zaman et al., 2013).

Ammonium-N concentration in the biochar treatment without N sources increased during the first week of incubation from 70 to 111 mg/kg soil (Fig. 1a). Compared to treatments without biochar (i.e., control treatments), the biochar treatments showed an increase in NH_4^+-N concentrations in all the N sources added soils. Application of biochar would have adsorbed NH_3 derived from N sources and if such adsorbed NH_3-N is extractable with 2 M KCl as NH_4^+-N, it would

explain the observed trend for higher NH_4^+-N concentration in the biochar treated soils (Taghizadeh-Toosi et al., 2011). Similar to the control treatments, urea with biochar treatment showed the highest NH_4^+-N concentration of 890 mg/kg soil on day 7, and the lowest concentration of 165 mg/kg soil was observed in GWC with biochar treatment on day 4 of the incubation period. Biosolids with biochar treatment showed a higher NH_4^+-N concentration of 572 mg/kg soil on day 7 than that from other OAs. In treatments with N sources in the presence of biochar addition, after day 42, NH_4^+-N concentration reached the concentration equivalent to that in the treatment without N sources (~20 mg/kg soil).

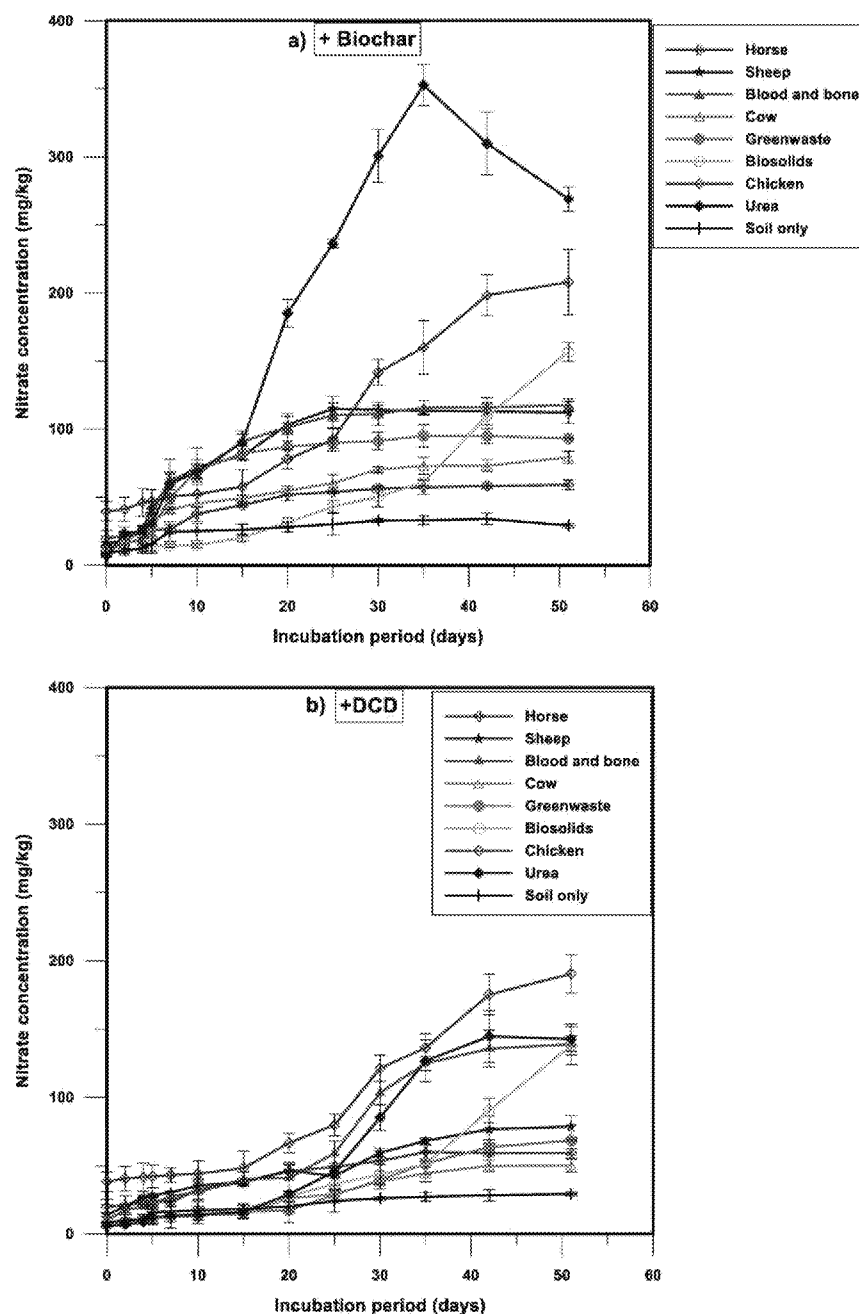Soils treated with DCD in the absence of N sources increased NH_4^+-N concentration during the first week of incubation (from 83 to 125 mg/kg) (Fig. 1b). Dicyandiamide did not have any effect on ammonification reaction, but showed significantly higher accumulation of soil NH_4^+-N compared to control treatments, which was probably due to the subsequent inhibition of conversion of NH_4^+-N to NO_3^--N by nitrification. A substantial increase in NH_4^+-N concentration in DCD treated soils with various N sources including fertilizers, manures, green waste, and biosolids has also been reported (Di and Cameron, 2004; Vogeler et al., 2007). Similar to the control treatment, urea added DCD treatment showed the highest NH_4^+-N concentration of 916 mg/kg soil on day 5, whereas the lowest of 170 mg/kg soil was observed in GWC with DCD treatment on day 4 of the incubation period. Biosolids with DCD treatment showed a higher NH_4^+-N concentration of 615 mg/kg soil on day 7 than that from other OAs. Ammonium-N concentrations in treatments with N sources in the presence of DCD were significantly higher by 4 fold even after day 51 of the incubation period than that in the control treatments with N sources ($P < 0.05$).

3.1.2. Nitrate concentration

During the 51 days of incubation study, among all the N sources, peak NO_3^--N concentration was observed in urea added biochar treatment (269 mg/kg soil). Among the organic N sources, the highest NO_3^--N concentration was observed in CM treatment (208 mg/kg soil) and the lowest in HM added biochar treatment (59 mg/kg soil). Biochar treatments showed lower nitrification rate and lower NO_3^--N concentrations than the control treatments (Table 3 and Fig. 2a). The possible reasons for this low NO_3^--N concentration in spite of high NH_4^+-N concentration in the biochar treatments (Fig. 1a) could include: (i) adsorption of NH_3 by the biochar, leading to a reduced soil NH_4^+-N pool available for nitrification (Taghizadeh-Toosi et al., 2011), and (ii) nitrification inhibition by the added biochar (Wang et al., 2012).

Clough and Condron (2010) found a volatile organic compound, α-pinene, in an unweathered biochar, and Sparks et al. (1996) found a non-volatile microbial inhibiting compound, ethylene, in various biochars added to the soil. These compounds can inhibit nitrification resulting in high NH_4^+-N accumulation and low NO_3^--N concentration in the soil. In the current study, though there was no prolonged occurrence of NH_4^+-N accumulation observed in the biochar treatment, NII results showed that biochar exhibited a slight inhibition activity (Fig. 3a). A gradual decrease in soil NO_3^--N concentration in some of the biochar treatments after day-35 could indicate: (i) the limited availability of NH_4^+-N in the soil (Fig. 1a), (ii) denitrification loss of N as N_2O or N_2 (iii) possible assimilatory reduction of NO_3^-, and/or (iv) consumption of NO_3^--N by soil microorganisms (Silver et al., 2001).

In treatments with N sources in the presence of DCD application, NO_3^--N accumulation was slow until day 30 of the incubation period as shown by lower nitrification rate when compared to the control treatments (Table 4). By the end of day 51, among all the N sources, peak NO_3^--N concentration was observed in CM added DCD treatment (191 mg/kg soil) and the lowest in CoM added DCD treatment (50 mg/kg soil) (Fig. 2b). Nitrification rate was significantly lower in N sources added DCD treatments than that in the N sources added control and biochar treatments, indicating that DCD delayed the oxidation of NH_4^+ to NO_3^-. Dicyandiamide inhibits or delays the process of nitrification of NH_4^+ to NO_3^-, thus decreasing the concentration of NO_3^--N in

Fig. 2. Nitrate-N concentrations in soils treated with and without organic and inorganic N sources in the presence of biochar (a) and DCD (b) over a period of 51 days. Each value represents a mean of three replicates with standard deviation shown by vertical bars.

the soil (Di et al., 2007). At the end of the incubation period, the mean values of NO_3^--N concentration in the soil with DCD were reduced by almost 50% (urea) and 21% (OAs) compared to that in the control treatments. This decrease in NO_3^--N in DCD treatments can be attributed to: (i) direct effect of DCD on nitrification inhibition (Singh et al., 2008), and (ii) increase in NH_4^+ salts in DCD treated soils that can inhibit nitrification (i.e., feedback mechanism) (Monaghan and Barraclough, 1992).

The NII calculated using Eq. (1) varied among the DCD treatments but increased with time in all of them and attained a peak value between days 10 and 20 (Fig. 3b). Maximum inhibition in the DCD treatment was found in urea amended soils (92%), followed by CoM (85%), GWC (84%), BB (74%), SM (63%), CM (30%), BS (31%) and HM (23%) amended soils. Singh et al. (2008) also found that the NII values for DCD applied at 10 mg/kg soil varied from 37%–66% in three different

soils when treated with N sources. The variation in nitrification inhibitory activity of DCD in the soils was attributed to a number of factors including OM content, soil pH, and aggregate size (Zhang and Feng, 2000).

3.1.3. Soil pH

Addition of N sources, to biochar or DCD treatments, increased the soil pH within a day and reached significantly higher values than that in the control treatments ($P < 0.05$). The addition of biochar and DCD increased the values of the mean soil pH by 0.10 and 0.25 units, respectively, relative to control treatments (Supplementary Information, SI 1). Wang et al. (2012) also noted an increase in soil pH by 0.22 unit in a rice (Oryza sativa) husk biochar treated upland soil. The pH of the soils amended with N sources and treated with biochar or DCD ranged from 6.87 to 8.83 and 7.18 to 8.97, respectively (SI 1). With the commencement of nitrification, in the biochar treatments, the pH decreased

Table 3

Nitrification rate (NR*) (mg NO_3^--N/kg soil/day) in soils treated with or without N sources in the presence of biochar (BC) application during the 51 days incubation period at room temperature.

Days	HM + BC	SM + BC	BB + BC	CoM + BC	GWC + BC	BS + BC	CM + BC	Urea + BC	Soil + BC
2	0.5	1.1	2.0	0.1	4.1	0.0	0.7	8.0	0.7
4	2.1	4.0	1.5	0.9	3.9	0.9	2.5	1.1	0.9
5	0.7	16.0	18.2	20.6	1.7	2.2	1.0	5.0	3.4
7	0.1	9.0	13.2	3.8	11.2	0.0	1.6	14.6	4.4
10	3.8	4.0	0.8	1.7	6.7	0.1	0.6	3.1	0.1
15	1.3	1.6	5.0	0.7	2.6	1.1	1.1	4.3	0.2
20	1.5	4.6	2.1	1.1	0.9	2.2	4.0	19.0	0.4
25	0.4	2.3	1.8	1.1	0.6	2.4	2.9	10.2	0.4
30	0.5	−0.1	0.2	2.0	0.3	1.4	9.9	12.9	0.6
35	0.2	−0.1	0.9	0.5	0.8	2.1	3.7	10.4	0.0
42	0.1	−0.1	0.1	0.0	0.0	6.9	5.5	−6.1	0.1
51	0.1	−0.1	0.2	0.7	−0.2	5.3	1.1	−4.5	−0.5

* $NR = \frac{N_f - N_i}{f - i}$ where, N_f and N_i are the total NO_3^--N mineralized (mg NO_3^--N/kg soil) in the biochar-soil mixture with or without N sources on the final and initial sampling dates, respectively; f and i are the final and initial sampling dates (day), respectively.
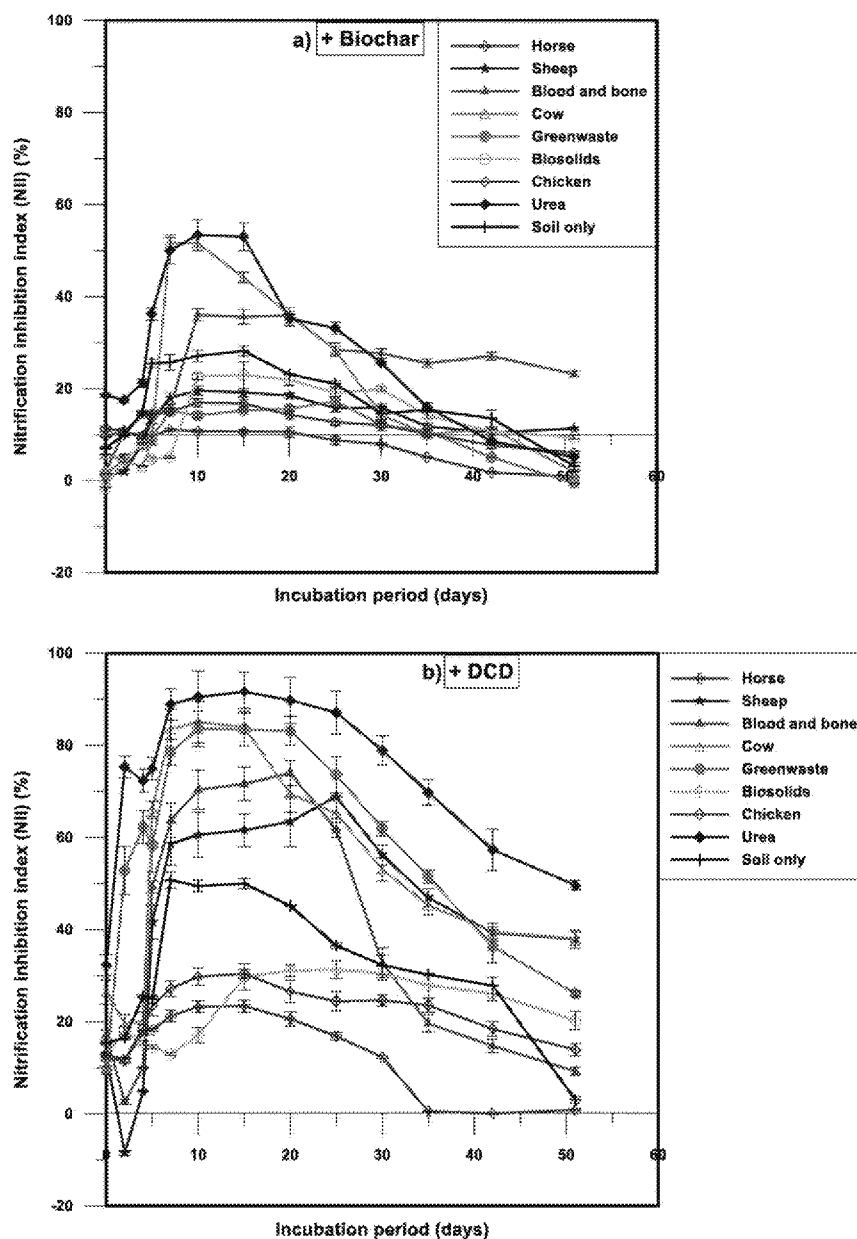
Fig. 3. Mean Nitrification inhibition index (NII*) (Eq.6.1) in soils treated with and without organic and inorganic N sources in the presence of biochar (7.18 mg C/kg soil) (a), and DCD (25 mg/kg) (b). Error bars represent the standard deviation of the three replicates. $NII = \frac{N_C - N_N}{N_C} \times 100$, where, N_N and N_C are the NO_3^--N concentrations in the N sources added soils in the presence and absence of biochar or DCD, respectively.

Table 4
Nitrification rate (NR*) (mg NO_3^--N/kg soil/day) in soils treated with or without N sources in the presence of DCD application during the 51 days incubation period at room temperature.

Incubation days	HM + DCD	SM + DCD	BB + DCD	CoM + DCD	GWC + DCD	BS + DCD	CM + DCD	Urea + DCD	Soil + DCD
2	0.5	3.1	3.7	0.4	0.1	0.0	1.2	0.5	0.7
4	1.1	3.5	1.3	0.7	0.9	1.1	0.5	1.0	0.5
5	0.6	1.3	2.1	2.1	2.0	1.7	0.5	3.0	5.1
7	−0.2	1.0	2.6	0.8	0.1	0.1	0.5	0.6	0.2
10	3.0	1.6	1.1	0.1	0.3	0.9	0.3	0.3	0.3
15	1.1	0.6	1.9	0.0	0.6	0.6	0.8	0.4	0.1
20	1.6	1.6	0.2	2.4	0.3	1.8	3.7	2.6	0.4
25	0.6	−0.8	3.6	0.6	2.3	1.8	2.6	3.3	0.8
30	0.9	3.4	8.9	1.9	2.2	1.4	8.3	7.9	0.4
35	1.3	1.7	4.3	1.2	2.4	1.5	3.0	8.3	0.2
42	−0.1	1.2	1.5	0.8	1.7	5.6	5.6	2.6	0.2
51	0.0	0.2	0.4	0.0	0.5	5.3	1.7	−0.2	0.1

* $NR = \frac{N_f - N_i}{f - i}$ where, N_f and N_i are the total NO_3^--N mineralized (mg NO_3^--N/kg soil) in the DCD-soil mixture with or without N sources on the final and initial sampling dates, respectively; f and i are the final and initial sampling dates (day), respectively.

sharply after the first week of the incubation, followed by a gradual decrease after day 35, but it was higher than the pH of the control treatments. In the DCD treatments, a gradual decrease in pH was noted after the peak value and compared to the control and biochar treatments, the pH remained significantly higher in the DCD treatments till the end of the incubation period ($P < 0.05$). Rise in soil pH with the application of N source is due to the production of hydroxyl (OH^-) ions through urea hydrolysis during the ammonification reaction (Eq. (3)), while the subsequent fall is associated with the production of hydrogen (H^+) ions during the nitrification reaction (Asing et al., 2008). A similar trend of rise followed by fall in pH values has been observed following the application of N sources by Asing et al. (2008) and Wang and Alva (1996). Laboratory incubation study by Singh et al. (2008) also showed that addition of DCD to soils amended with N sources resulted in increased soil pH followed by a gradual and slower decrease in soil pH than the soils treated with N sources only. The higher pH in the presence of DCD and biochar application is attributed to the lower rate of the release of protons due to the inhibition of nitrification reaction.

3.2. N gaseous losses

3.2.1. Ammonia volatilization

The NH_3 volatilization data of the biochar treated soils indicated that the emission peaked within the first 10 days of the incubation period, and the highest peak of 20 mg N/kg was measured in urea added biochar treatment on day 10 of the incubation period. Among OAs added biochar soils, maximum peaks were observed in BS soil (14 mg N/kg) followed by CM (12 mg N/kg soil), SM (11 mg N/kg soil), BB (10 mg N/kg), CoM (9 mg N/kg), HM (8 mg N/kg), and GWC (6 mg N/kg) on day 10, 7, 10, 10, 7, 10, and 10 of the incubation period, respectively. In all the biochar treatments, the peak emissions were observed within the first 10 days of the incubation period and the emissions rapidly reached the background level after the second week of the incubation study. No emissions were observed after day 20 in all the biochar treatments.

Cumulative emission of 39 mg N/kg soil was observed in urea added biochar treatment against 69 mg/kg in the urea added soils alone (Fig. 4a). Among the OAs, the highest cumulative NH_3 emission of 30 mg/kg soil was observed in BS added biochar treatment and the lowest in GWC added biochar treatment (11 mg/kg). Cumulative N loss as NH_3-N in the biochar treatments followed in the order of: Urea > BS > SM > CM > BB > CoM > HM > GWC. The total amount of N lost as NH_3 as a percentage of N added in HM, SM, BB, CoM, GWC, BS, CM, and urea added biochar soils were 3.0, 8.0, 5.8, 4.3, 1.7, 8.6, 6.9, and 11.3%, respectively. The total amounts of N loss as NH_3 in the HM, SM, BB, CoM, GWC, BS, CM, and urea added soils without biochar were 3.0, 11.9, 9.6, 5.4, 2.1, 15.7, 13.1, and 19.3%, respectively.

Maximum emission reduction (47%) was obtained in CM added biochar soils, with cumulative emissions reduced from 39 to 21 mg/kg soil.

The lowest reduction percent was observed in HM added biochar treatment (7.4%). In HM, SM, BB, GWC, BS, and urea amended biochar soils, emission reductions of 33, 39, 21, 18, 45, and 42% were observed, respectively. On average, the addition of biochar significantly reduced NH_3 loss by 32% when compared to the control treatments. These results agree with the short-term laboratory incubation findings of Doydora et al. (2011) in which NH_3 volatilization was reduced from poultry litter in soils treated with various biochars. However, it was expected that the addition of biochar with high pH (pH - 10.08) might stimulate NH_3 loss from the N sources amended soils (e.g., DeLuca et al., 2009). Ammonia volatilization did occur in some of the biochar treatments, but the rates were very low when compared to the control treatments (Fig. 4a). Similar results of reduced NH_3 loss from N sources amended soils after addition of high pH biochar (pH - 9.83) obtained by Jones et al. (2012) was attributed to the binding of NH_4^+ to biochar cation exchange sites and subsequent neutralization of carbonates and alkaline oxides in the biochar (Le Leuch and Bandosz, 2007).

Physical properties such as surface area and pore structure of the biochar are reported to influence the interaction of biochar with soil microorganisms and nutrient cycling (Chen and Chen, 2009; Kasozi et al., 2010; Lammirato et al., 2011). Given the pore size (30.3 nm - mesopore) and the surface area (104.68 m^2/g) of the biochar used in this study (Table 2), this biochar could provide sites for the deposition of clay nanoparticles, dissolved organic matter, and nutrients including N, P, and K (Lehmann and Joseph, 2009). In view of the small size of NH_3 (2.56 Å), the biochar used in this study was well suitable for the adsorption of NH_3 onto its surface and into the pores (Doonan et al., 2010). After 51 days of the incubation study, the pore size of the biochar was reduced to a greater extent than the fresh biochar (SI 2). This pore size reduction can be due to the interaction of the organic matter and microorganisms with its surfaces (Kwon and Pignatello, 2005).

Beyond physical properties, the chemistry of the surface functional groups on biochar provides greater control over chemical sorption of solutes by biochars (Fletcher et al., 2007; Hina et al., 2010; Uchimiya et al., 2011). Qualitative analysis of surface functional groups using FTIR showed a peak at 1588.6 cm^{-1} (SI 3) indicating the presence of stretching vibration of conjugated C=C bonds and —COOH groups (Hsu et al., 2009). The bands at 1380.7 cm^{-1} and at 1115.1 cm^{-1} are attributable to vibration of C—O bond in skeletal ring and stretching of C—C bond, respectively (Shen et al., 2010). The presence of acidic functional groups, oxygen-containing groups in particular, on the surface of the biochar enhances the sorption of NH_3 (Spokas et al., 2012), demonstrating the sorption capacity of the biochar used in this study.

In DCD treated soils, the NH_3 volatilization peaked within 5 days of the incubation period with the highest peak emission (37 mg N/kg) measured on day 5 from urea amended DCD treatment, followed by BS (30 mg N/kg), CM (23 mg N/kg), SM (16 mg N/kg), CoM (16 mg N/kg), BB (13 mg N/kg), GWC (9 mg N/kg), and HM (9 mg N/kg) amended DCD soils on day 7, 5, 4, 4, 5, 5, and 5 of the
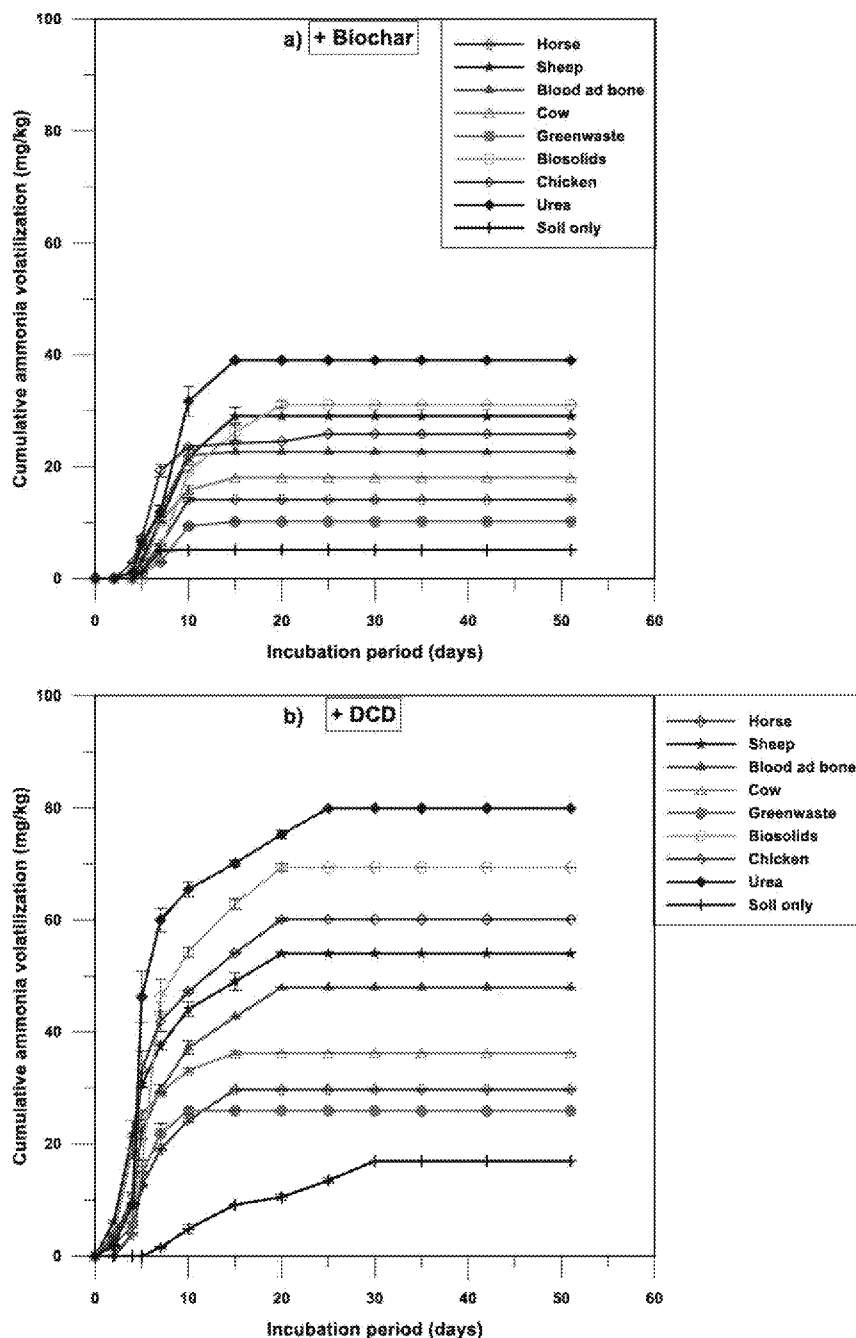
Fig. 4. Cumulative ammonia (NH₃) emissions in soils treated with and without organic and inorganic N sources in the presence of biochar (a) and DCD (b) application over a period of 51 days. Each value represents a mean of three replicates with standard deviation shown by vertical bars.

incubation period, respectively (Fig. 4b). The majority of NH₃ emissions occurred within the first week of the incubation period, because of the high soil pH during ammonification and NH₄⁺-N accumulation (SI 1 and Fig. 1b) (Saggar et al., 2004a).

The highest cumulative NH₃ emission was observed from urea added DCD treatment (69 mg N/kg) compared to other N sources amended DCD treatments (Fig. 4b). Among OAs, BS added DCD treatment showed the highest cumulative emission of 67 mg N/kg soil and the lowest was observed in GWC added DCD treatment (26 mg N/kg). In HM, SM, BB, CoM, and CM added DCD soils, cumulative NH₃ emissions of 30, 54, 48, 3, and 58 mg/kg, respectively were measured. The total amount of N loss as NH₃ emissions in HM, SM, BB, CoM, GWC, BS, CM, and urea added DCD soils were 4.3, 2.4, 10.4, 6.4, 3.0, 17.5, 14.4, and 21.0%, respectively. As the magnitude of the NH₃ emission from N

sources can be affected by a number of soil and environmental properties (pH, cation exchange capacity, nitrification activity, soil moisture, and soil temperature), a wide range of losses as a percentage of the applied N [e.g., 6–28% by Soares et al., 2012; 1.7–5.7% by Zaman et al., 2008; and 4–27% by Lockyer and Whitehead, 1990] have been reported in the literature.

Addition of DCD significantly increased N loss as NH₃ in all the soils compared to the control and biochar treatments. In HM, SM, BB, CoM, GWC, BS, CM, and urea amended DCD soils, emissions were increased by 32, 4, 8, 18, 45, 11, 10, and 9%, respectively, when compared to control treatments, and by 30, 36, 44, 33, 44, 51, 52, and 46%, respectively, when compared to biochar treatments. On average, the addition of DCD to N sources amended soils increased NH₃ volatilization by 17 and 42% when compared to control and biochar treated soils,

respectively. This enhanced NH_3 emission from N sources in the presence of DCD was attributed to its nitrification inhibitory activity, delaying the conversion of NH_4^+ to NO_3^- and thus resulting in accumulation of large amounts of NH_4^+. Similar increases in NH_3 emission from N sources added soil in the presence of DCD were previously reported (Asing et al., 2008; Zaman et al., 2013).

Soil pH is one of the important factors that control NH_3 emission. Hence in both the biochar and DCD treated soils, the relationship between soil pH and cumulative amount of NH_3 volatilization was also investigated. The regression analysis was undertaken with the peak soil pH attained during the incubation of biochar or DCD with N sources and NH_3 volatilized (Fig. 5). The strongly significant correlation coefficients ($R^2 = 0.87$ for biochar and $R^2 = 0.86$ for DCD at $P < 0.05$) clearly indicated that elevated soil pH enhanced NH_3 volatilization from the biochar and DCD treated soils (Eq. (4)). There exists a strong relationship between peak NH_4^+-N concentration and NH_3 volatilization in both biochar and DCD treated N sources amended soils ($R^2 = 0.89$ for biochar and $R^2 = 0.95$ for DCD at $P < 0.05$) (SI 4). The higher the NH_4^+-N concentration, the higher was the NH_3 volatilization from the biochar or DCD treated soil.

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \qquad (4)$$

3.2.2. Nitrous oxide emission

Addition of N sources to biochar treated soils increased total N_2O-N emission when compared to the biochar treatment without any additional N sources. Maximum emission of N_2O from N sources added biochar soils occurred during the first week of the incubation period (Fig. 6a) followed by smaller peaks in the second week of the incubation period. Little or no emissions were observed after day 20 of the incubation period. Initial peaks after biochar addition confirm that biochar-induced N_2O emissions are usually episodic and short-lived.

Among all the added N sources, urea added biochar soils showed significantly higher N_2O emission with a peak emission of 9.2 mg N/kg soil on day 7 of the incubation period ($P < 0.05$). Among the organic N sources added to biochar treatments, the highest N_2O emission peak was measured in the BS soil (5.1 mg N/kg), followed by CM (3.6 mg N/kg), BB (3.4 mg N/kg), SM (3.3 mg N/kg), CoM (2.9 mg N/kg), HM (2.5 mg N/kg), and GWC (2.4 mg N/kg) added soils. Similarly, the total N_2O-N emission from N sources amended biochar soils followed in the order of: urea > BS > CM > SM > BB > CoM > HM > GWC. The percentage of applied N lost as N_2O emissions

Fig. 6. Nitrous oxide emissions in soils treated with and without organic and inorganic N sources in the presence of biochar (a) and DCD (b) application over a period of 51 days. Each value represents a mean of three replicates with standard deviation shown by vertical bars.

in HM, SM, BB, CoM, GWC, BS, CM, and urea added biochar soils were 1.27, 1.51, 1.28, 1.36, 1.13, 2.45, 1.58, and 5.35%, respectively. The percentage of applied N lost as N_2O in the HM, SM, BB, CoM, GWC, BS, CM, and urea added soils without biochar were 31.3, 2.0, 1.8, 1.4, 1.2, 3.3, 2.3, and 6.9%, respectively.

Addition of biochar significantly reduced peak emissions in all the soils compared to the emissions from control treatments ($P < 0.05$). Maximum emissions reduction (30%) was obtained in CM added soils, with cumulative emissions reducing from 6.77 to 4.73 mg N/kg in the biochar treatment. In HM, SM, BB, GWC, BS, and urea amended biochar soils, emission reductions of 4.76, 25.29, 27.87, 8.36, 24.87, and 22.73%,
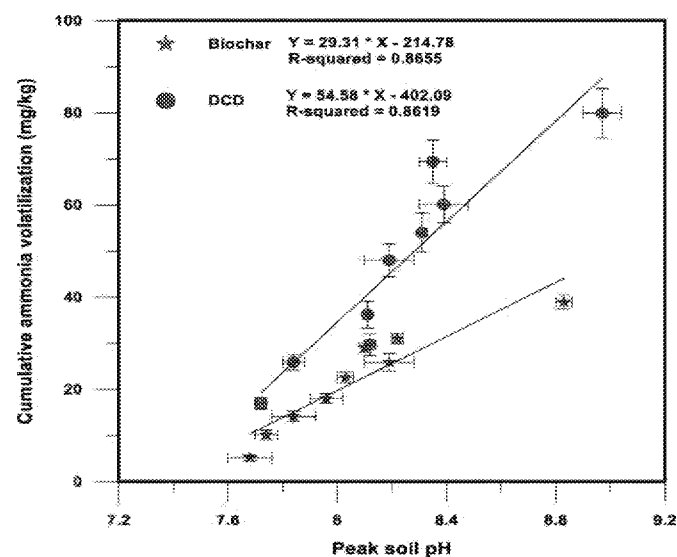

Fig. 5. Regression relationships between peak soil pH attained during the incubation of various N sources with biochar/DCD and the cumulative ammonia (NH_3) volatilization.
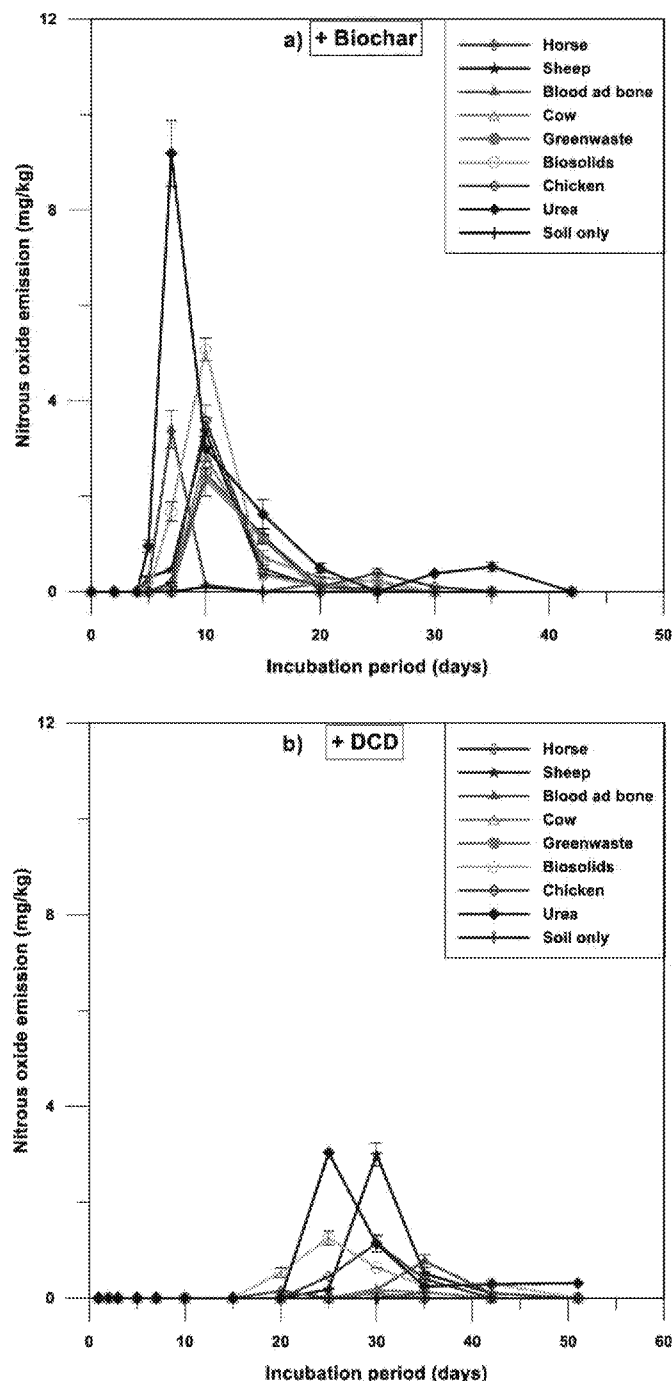
were observed, respectively. The lowest reduction percent was observed in CoM added soil biochar treatment (3.09%). On average, the addition of biochar reduced N_2O-N emission from N sources added soils by 18.4% when compared to the control treatments. The N_2O emissions in the biochar treatment without any N source remained constant throughout the incubation period with N_2O-N loss ranging from 0.08 to 0.12 mg N/kg soil.

There are reports of reduced N_2O emissions associated with biochar treatments to agricultural soils (Singh et al., 2010; Spokas et al., 2009; Van Zwieten et al., 2010). Two possible explanations for reduced N_2O loss from biochar treated soils in this study include reduced denitrification and/or complete denitrification. A decrease in NH_4^+ concentration for nitrification, leading to the lack of substrate (NO_3) for subsequent denitrification, would result in reduced N_2O emission. Also, the addition of biochar increased the aeration thereby causing low denitrification in the soil (Fig. 6a) (Rondon et al., 2005; Taghizadeh-Toosi et al., 2011; Yanai et al., 2007). Furthermore, Mizuta et al. (2004) and Taghizadeh-Toosi et al. (2011) indicated that sorption of NO_3^- to biochar resulted in low substrate availability for denitrification and subsequent reduction in N_2O emission.

Another theory to explain the low N_2O emission from biochar treated soil is complete denitrification resulting in N_2 emission rather than N_2O. Enhanced microbial activity, in particular denitrifier communities such as Bradyrhizobiaceae and Hyphomicrobiaceae would have potentially increased denitrification rate resulting in N_2 emission (Anderson et al., 2011). The alkaline nature of biochar (pH 10.08) would increase the activity of N_2O-reductase enzyme, enhancing complete denitrification (Singh et al., 2010; Van Zwieten et al., 2010). Addition of labile C and N with the biochar and N sources would rapidly increase soil microbial biomass C, which further depletes O_2, creating an anoxic environment in the soil leading to complete denitrification (Nguyen and Lehmann, 2009).

Addition of N sources to DCD treated soils increased N_2O emissions when compared to DCD soils without any N sources. The highest N_2O emission peak was observed in the urea added DCD soil (3.03 mg N/kg) (Fig. 6b). Among the organic N sources added to DCD treatments, the highest N_2O emission peak was measured in the SM amended soil (2.99 mg N/kg), followed by BS (1.25 mg N/kg), CM (1.14 mg N/kg), BB (0.77 mg N/kg), CoM (0.16 mg N/kg), and HM (0.12 mg N/kg). Likewise, the cumulative N_2O-N emission from N sources amended DCD soils followed in the order of: urea > SM > BS > CM > BB > CoM > HM > GWC. The total amount of N lost as N_2O emissions as a percentage of N added in HM, SM, BB, CoM, GWC, BS, CM, and urea added biochar soils were 0.04, 1.26, 0.40, 0.09, 0.03, 0.99, 0.66, and 1.67%, respectively. The total amounts of N loss as N_2O in the HM, SM, BB, CoM, GWC, BS, CM, and urea added soils without DCD were 1.3, 2.0, 1.8, 1.4, 1.2, 3.3, 2.3, and 6.9%, respectively.

Addition of DCD significantly reduced peak emissions in all N treated soils compared to the emissions from control treatments. Nitrification inhibitors delay the oxidation of NH_4^+ to NO_3^- by depressing the activities of nitrifiers in the soil (Hatch et al., 2005); thus, it can reduce N_2O emission directly by decreasing nitrification or indirectly by reducing the availability of NO_3^- for denitrification. Maximum emissions reduction (97.30%) was obtained in GWC added soils, with cumulative emissions reducing from 3.72 to 0.10 mg N/kg in the DCD treatment. In HM, BB, CoM, BS, CM, and urea added DCD soils, emission reductions of 96.99, 77.40, 93.35, 69.60, 70.67, and 75.93%, were observed, respectively. The lowest reduction percent was observed in SM added DCD soil (37.52%). These reduction percentages are comparable to the 43% reduction in emissions obtained by Majumdar et al. (2000) in urea plus DCD treated soils. However, Hatch et al. (2005) and Merino et al. (2002) observed higher N_2O reduction percentages of 96 and 100%, respectively, when DCD was applied to slurry treated soils. These differences in N_2O emission reduction by DCD among the N sources are probably due to: (i) physical separation of the inhibitor and N source during the early part of the experiment in the soil, and/or (ii) lack of infiltration of DCD in all the sites where nitrification was most active (Hatch et al., 2005).

Nitrogen substrate either as NH_4^+-N or NO_3^--N is one of the important factors controlling N_2O emission. There exists a strong correlation between NH_4^+-N concentration and N_2O emission from biochar and DCD treated soils ($R^2 = 0.84$ for biochar and $R^2 = 0.86$ for DCD) (SI 5). Though the magnitude of the emissions varied between biochar and DCD treatments, the emissions increased with an increase in NH_4^+-N concentration in the soils. The difference in N_2O emission between biochar and DCD treated soils could be attributed to the difference in NH_4^+-N concentrations between these two amendments.

When compared to biochar treatments, addition of DCD significantly reduced N loss as N_2O emissions. Highest emission reduction percentage was observed in GWC (97.06%) added DCD soil, followed by HM (96.84%), CoM (93.14%), urea (68.85%), BB (68.67%), BS (59.54%), CM (58.04%), and SM (16.37%) added DCD soils. On average, DCD reduced N loss as N_2O by 69.81% when compared with biochar treatments. The mean values of N_2O emitted as a percentage of the applied N in this DCD study (0.64%) were comparable to those of other researchers (De Klein et al., 2003; Luo et al., 2008). In general, the effect of DCD lasted for 35 days as shown by the rapid increase in NO_3^--N concentration in some of the N sources added soils and the decrease in NII values after day 35 (Fig. 3b). This can be explained by the fact that breakdown of DCD by soil microorganisms repopulates the soil with nitrifiers and hence increases nitrification rate (Singh et al., 2008). Depending upon soil moisture, temperature, organic matter, clay content, microbial activity, and pH, the nitrification inhibitory effect of DCD usually lasts between 4 and 10 weeks (Singh et al., 2008).

3.3. N recovery

The total N recovered from biochar treatments varied from 39.55 to 97.55% and in DCD treatments, the total N recovered ranged from 23.79 to 111.95% (Fig. 7a and b; Table 5). For all the N sources added control treatments, the percentage of N loss as NH_3 ranged from 2.06 to 19.32%, whereas when biochar was added, the percentage of N loss as NH_3 was reduced to 1.68–11.29%. Similarly, the addition of biochar decreased the percentage of N loss as N_2O by 1.13 to 5.35% when compared to the control treatments (1.24 to 6.92%).

The percentage of N lost as NH_3 increased from 3% to 21% in the DCD treatments, when compared to the control treatments. However, the percentage of N loss as N_2O decreased with the addition of DCD to the N sources added soils. Dicyandiamide addition to the N sources added soils (i.e., HM, SM, BB, CoM, GWC, BS, CM, and urea) decreased the percentage of N lost as N_2O from 1.33 to 0.04, 2.02 to 1.26, 1.77 to 0.40, 1.40 to 0.09, 1.24% to 0.03, 3.25 to 0.99, 2.25 to 0.66, and 6.92 to 1.67%, respectively (Fig. 7b).

The total N recovered as NH_4^+ and NO_3^- in biochar and DCD treatments ranged from 15.30 to 80.92% and from 17.28 to 103.56%, respectively. Biochar reduced total N loss as NH_3 and N_2O in HM, SM, BB, CoM, GWC, BS, CM, and urea amended soils by 6.59, 31.93, 37.65, 17.22, 14.57, 41.52, 44.81, and 36.61%, respectively, when compared to control treatments. On average, addition of biochar reduced total N loss as NH_3 and N_2O by 28.87% in all the N sources amended soil when compared to the control treatments. Dicyandiamide treatments reduced total N loss in HM, SM, BB, CoM, GWC, BS, CM, and urea amended soils by 5.71, 2.01, 5.65, 4.63, 8.20, 2.50, 1.94, and 13.63%, respectively, when compared to the control treatments. On average, addition of DCD reduced total N loss by 5.53% in all the N sources amended soil. When comparing the effect of biochar and DCD in reducing N loss from soils amended with various N sources, biochar reduced the N loss in HM, SM, BB, CoM, GWC, BS, CM, and urea amended soils by 0.93, 30.54, 33.92, 13.20, 6.95, 40.02, 43.72, and 26.61%, respectively. Thus the macadamia nut shell biochar used in this study was more effective in reducing the gaseous N loss through NH_3 and N_2O emissions by 24.49% when compared to DCD.
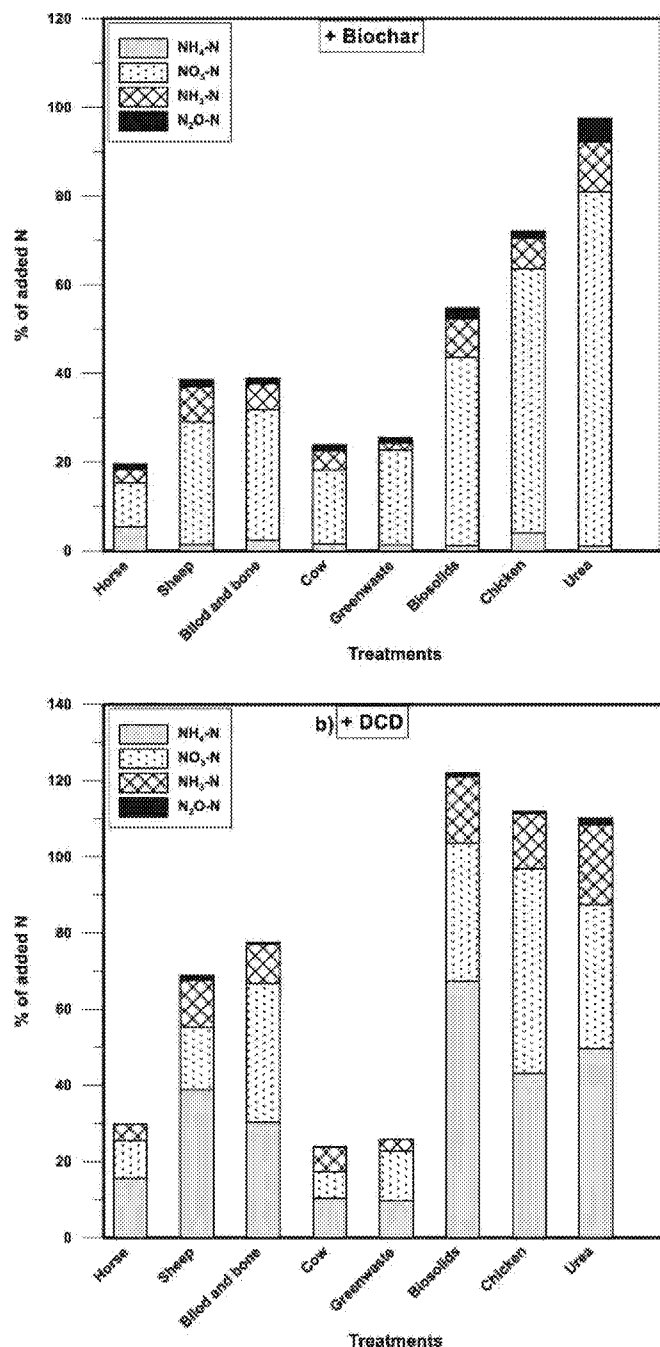
Fig. 7. Percentage of N fractions of total N recovered in soils treated with and without organic and inorganic N sources in the presence of biochar (a) and DCD (b) application at the end of the incubation period (51 days).

4. Conclusions

This study showed that N is lost through NH_3 volatilization and N_2O emissions from both organic and inorganic N sources, which is more pronounced in case of inorganic N sources. DCD was more effective in decreasing N_2O emissions from applied N sources in an agricultural soil when compared to biochar. However, DCD addition resulted in an increase in NH_3 emission from soil. Biochar decreased both NH_3 and N_2O emissions following the application of various N sources as compared to DCD treatments. Although DCD application resulted in a much higher reduction of N_2O emission compared to biochar, the latter was effective in decreasing total N loss through NH_3 and N_2O emissions by 25% when compared to DCD. Hence biochar can be used as an

Table 5
The amount of N (mg/kg soil) as NH_4^+ and NO_3^- in the soil, N lost as NH_3 and N_2O following the application of various N sources with biochar and DCD.

Biochar	NH_4	NO_3^-	NH_3	N_2O	Total N recovered
HM + biochar	16.0	29.8	8.95	3.80	58.6
SM + biochar	4.10	83.0	23.8	4.52	115
BB + biochar	7.01	88.3	17.4	3.83	116
CoM + biochar	4.57	50.0	12.8	4.08	71.5
GWC + biochar	4.02	63.9	5.04	3.40	76.3
BS + biochar	3.62	127	25.9	7.34	164
CM + biochar	12.0	178	20.6	4.73	216
Urea + biochar	3.00	239	33.8	16.0	292
HM + DCD	46.7	29.8	12.7	0.12	89.4
SM + DCD	116	49.3	37.0	3.78	206
BB + DCD	90.7	109	31.0	1.20	232
CoM + DCD	31.0	20.8	19.2	0.28	71.3
GWC + DCD	28.8	39.1	8.90	0.10	77.0
BS + DCD	202	108	52.4	2.97	366
CM + DCD	129	161	43.1	1.98	335
Urea + DCD	148	113	63.0	5.00	330

alternative source of nitrification inhibitor thereby mitigating the gaseous loss of N through NH_3 volatilization and N_2O emissions.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.08.242.

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